Do Binary Hard Disks Exhibit an Ideal Glass Transition?

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We demonstrate that there is no ideal glass transition in a binary hard-disk mixture by explicitly constructing an exponential number of jammed packings with densities spanning the spectrum from the accepted "amorphous" glassy state to the phase-separated crystal. Thus the configurational entropy cannot be zero for an ideal amorphous glass, presumed distinct from the crystal in numerous theoretical and numerical estimates in the literature. This objection parallels our previous critique of the idea that there is a most-dense random (close) packing for hard spheres [*Torquato et al, Phys. Rev. Lett., 84, 2064 (2000)*].

Understanding the glass transition in dense or supercooled liquids remains one of the challenges of condensed matter physics. In particular, considerable effort has been directed at identifying the cause of the dramatic slowdown of the dynamics in the vicinity of the kinetic glass transition, as evidenced in a decrease of the diffusion coefficient and an increase in relaxation times. One possibility is that a thermodynamic transition different from the usual liquid-solid transition underlies the kinetic one. One scenario originally suggested by Adam and Gibbs [1] relates the slow diffusion to a vanishing of the number of alternative configurations available to the liquid, leading to an *ideal thermodynamic glass transition* when the liquid has no choice but to remain trapped in one of few glassy configurations. An important basic assumption in these considerations is that crystalline configurations, which are thermodynamically favored, are kinetically inacessible and therefore the liquid is restricted to exploring "amorphous" configurations. In particular, the term amorphous has become implicitly attached to the term glass, and crystalline configurations have been assumed to be qualitatively different from glassy ones. In this Letter, we study a specific model glass former, namely, a binary hard disk mixture, and show that, for this model, the presumed "ideal glass" is in fact a phase-separated crystal, and that that there is no special amorphous (random) state, but rather a continium of states from the most disordered one to the most ordered one [2].

An inherent-structure formalism was proposed by Stillinger and Weber and has since been used extensively in the analysis of the thermodynamics of supercooled liquids [3]. The "inherent-structures" of hard-particle systems are in fact (collectively) *jammed packings* [4], which are mechanically stable packings where the particles are trapped in a static configuration despite thermal or external agitation. For soft-particle systems, an essential quantity in this thermodynamic analysis is the number of distinct energy minima (basins) with a given energy per particle. For hard-particle systems this becomes the number of distinct jammed packings $N_g(\phi_J) = \exp\left[N s_c(\phi_J)\right]$ with jamming packing fraction (density) ϕ_J, where $s_c(\phi_J)$ is the *configurational entropy* (degeneracy) per particle. It is assumed that the liquid remains in the vicinity of these basins for long periods of time, jumping from one basin to another as it explores the available configuration space. Denser packings are favored in terms of their free-volume; the most favored one being the crystal of density $\phi_{\max}$. However, it is reasonable to assume that the degeneracy $s_c(\phi_J)$ decreases with increasing ϕ_J. The liquid achieves minimum free energy by trading off degeneracy for free volume, so that at a given density ϕ it predominantly samples glasses with jamming density $\hat{\phi}_J(\phi)$. The conjectured ideal glass state corresponds to the point where the number of available basins becomes subexponential, that is, $s_c(\phi_J^{\mathrm{IG}}) = 0$. At densities above an ideal glass transition density ϕ_{IG}, defined via $\phi_J(\phi_{\mathrm{IG}}) = \phi_J^{\mathrm{IG}}$, the liquid becomes permanently trapped in the ideal glass state. A crucial unquestioned assumption has been that $\phi_J^{\mathrm{IG}} < \phi_{\max}$, i.e., that there is a gap in the density of jammed states between the amorphous and crystal ones. We will explicitly show that this assumption is flawed for the binary hard-disk mixture we study, and suggest that this is the case in other similar models, contrary to numerous estimates for ϕ_J^{IG} in the literature [5, 6, 7].

Previous simulations have cast doubt on the existence of ideal glass transitions in hard-particle systems [9, 14]. In particular, it has already been suggested that the slope of $s_c(\phi_J)$ at ϕ_J^{IG} dramatically affects the location of the presumed transition; an infinite slope shifts the transition to zero temperature [10]. Questions have also been raised about the validity of extrapolations into temperature/density regions that are inacessible to accurate computer simulations [11], as well as the impact of finite-size effects [12]. In this Letter, we present clear evidence that the concept of an ideal glass transition is flawed for distinctly different reasons. Specifically, for our model, we *explicitly* construct an exponential number of jammed packings with jamming densities ϕ_J that span from the accepted "amorphous" state with $\phi_J^g \approx 0.84$ to that of the crystal, with $\phi_{\max} = \pi/\sqrt{12} \approx 0.91$, thus clearly showing that the configurational entropy cannot be zero for the hypothetical most-dense amorphous (ideal) glass distinct from the crystal. This objection is in the same spirit as the critique of the concept of random close packing (RCP) raised by one of us in Ref. [2], namely, that there is a continuous tradeoff between disorder (closely

linked to degeneracy) and density, making the definition of a most-dense random packing ill-defined. Instead, Ref. [2] replaces RCP with the maximally random jammed (MRJ) state, i.e., the most disordered of all jammed states.

Here we study a binary mixture of disks with a third (composition $x_B = 1/3$) of the disks having a diameter $\kappa = 1.4$ times larger than the remaining two thirds ($x_A = 2/3$). Bidisperse disk packings with this aspect ratio and $x_A = x_B = 1/2$ have been studied [21] as model glass formers [13]. For this κ, it is believed that the high-density phase is a phase-separated crystal. Our free-energy calculations predict that at the freezing density $\phi_F \approx 0.775$, a crystal of predominantly large particles should start precipitating from the liquid mixture, i.e., systems in true thermodynamic equilibrium should crystallize just like the equivalent monodisperse system. Nucleation is however kinetically strongly suppressed due to the need for large-scale diffusion of large disks toward the nucleus [14], and in fact, we have not observed crystallization even in simulations lasting tens of millions of collisions per particle well above the estimated freezing density.

The quantity $N_g(\phi_J)$ has recently been estimated via explicit enumeration for binary mixtures of relatively small numbers of hard disks [15]. These studies have observed an approximately Gaussian $N_g(\phi_J)$ that is peaked at a density $\phi_{\mathrm{MRJ}} \approx 0.842$, interpreted to correspond to the MRJ state for this system. Such a Gaussian $N_g(\phi_J)$ corresponds to an inverted parabola for $s_c(\phi_J)$, as has been assumed in previous studies of the thermodynamics of binary disk glasses [5]. For large systems, such enumeration is not yet possible and thermodynamics has been used to obtain estimates of $s_c(\phi_J)$, namely, it is estimated as the difference between the entropy (per particle) of the liquid $s_L(\phi)$ and the entropy of the "glass" $s_g(\phi)$, $s_c\left[\hat{\phi}_J(\phi)\right] = s_L(\phi) - s_g(\phi)$. Here s_L is obtained via thermodynamic integration of the *equilibrium* liquid equation of state (EOS) from the ideal gas limit, while s_g is defined as the entropy of the system constrained to vibrate around a single basin with jamming density ϕ_J, without the possibility of particle rearrangements. There is significant ambiguity in definining these constraints; however, at least in the truly glassy region, the system is typically spontaneously constrained (jammed) by virtue of a very slow rearrangement dynamics, so that s_g can be defined reasonably precisely.

We have calculated $s_g(\phi)$ using a collision-driven molecular dynamics (MD) algorithm that will be described in detail in a future publication [16]. For hard disks, it is very similar to the tether method of Speedy [5]. The particles are restricted to remain inside hard-wall cells in the vicinity of their initial configuration. The cells are initially about twice as large as a particle (in linear dimension), which allows particle vibrations but restricts particle rearrangements, and has been assumed to define s_g. The cells then shrink in size slowly during the course of the MD run, and at the end they become disjoint, leading to a non-interacting system of particles with analytically-known free energy. The work done to shrink the cells then gives the initial entropy of the glass. Closely related methods have previously been used to calculate configurational entropy [5, 6], with similar, though less accurate results. For soft-particle glasses, an alternative method is to use the harmonic approximation to the vibrational entropy at an energy minimum as an estimate of s_g [5, 6]. Both methods are rigorous only in the high-density (jamming) or $T \to 0$ limit, and are approximate for liquids, so the quantitative results at low ϕ should be interpreted with caution.

The calculation of the true equilibrium liquid equation of state (EOS) is not possible inside the glassy region with conventional simulation methods, especially for large system sizes [11, 12, 17]. In our MD algorithm, we produce glasses by starting with a low-density liquid and growing the particle diameters at a growth rate $\gamma = dD/dt \ll 1$ [4], for a very wide range of compression rates γ. Instead of looking directly at the reduced pressure $p = PV/NkT$, we assume that a free-volume EOS [4] holds approximately and estimate the jamming density $\hat{\phi}_J(\phi)$ from the instantaneous pressure

$$\tilde{\phi}_J = \frac{\phi}{1 - 2/p(\phi)}.$$

In the jamming limit ($p \to \infty$), we get that $\tilde{\phi}_J = \phi = \phi_J$, and close to jamming $\tilde{\phi}_J \approx \phi_J$, and thus it is much more useful to plot $\tilde{\phi}_J(\phi)$ instead of $p(\phi)$. This is evident in Fig. 1, where we show $\tilde{\phi}_J(\phi)$ for a range of γ's. We see that fast compressions fall out of equilibrium at lower kinetic glass-transition densities ϕ_g, and that the nonequilibrium glassy EOS is very well described by an empirical $\tilde{\phi}_J = (1 + \alpha)\phi_J - \alpha\phi$, where $\alpha \approx 0.133$, over a wide range of $\phi > \phi_g$. It is also clear that even for the slowest compressions $\phi_g \approx 0.8$, so that equilibrating the liquid in reasonable time is not possible beyond this "kinetic glass-transition" density. Very long MD runs, with as many as 50 million collisions per particle, have failed to equilibriate our samples at a fixed $\phi = 0.8$, and in fact very different microstructures all remained stable for very long periods of time.

The final jamming densities of the glasses compressed at different rates are shown in Fig. 2. Note that slower compressions consistently yield denser packings with no hints of the existence of a *densest* glass. Fast compressions produce packings that are not truly jammed [4] and subsequent relaxation of these systems increases the density to around $\phi_J \approx 0.847$. This behavior of our hard-disk systems is closely related to the observation that supercooled liquids sample saddle points with the saddle index diminishing only below the temperature where even the slowest cooling schedules fall out of equilibrium [18], i.e., the kinetic glass transition temperature. Observations similar to those in in Fig. 2 have already been made for systems of soft particles, e.g., the energy of the lowest inherent-structure sampled has been shown to continuously decrease for slower cooling [3].

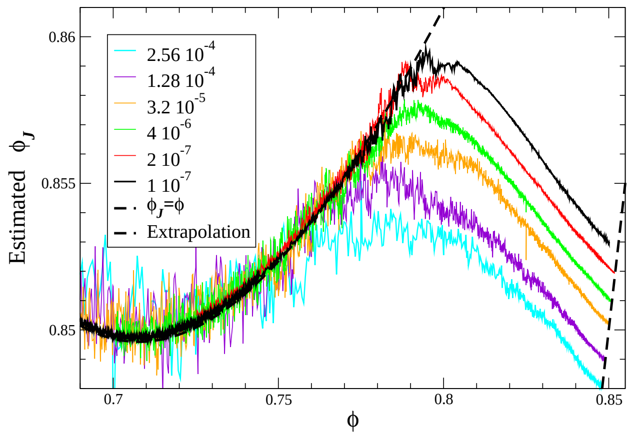


Figure 1: The equation of state $\tilde{\phi}_J(\phi)$ for $N = 4096$ disks as observed by compressing a liquid with different expansion r

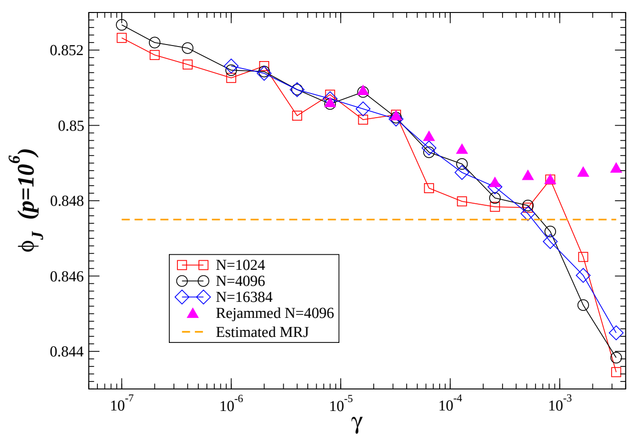


Figure 2: Final jamming densityϕ_J for different compression rates γ, with and without additional relaxation to ensure a truly jammed packing has been reached.

The measured $s_c(\phi)$ for the different glass compressions are shown in Fig. 3. For comparison, the results for a slow compression of a monodisperse system are also shown and the entropy of mixing $s_{\mathrm{mix}} = x_A \ln x_A + x_B \ln x_B$ has been subtracted from s_c. It is seen that for the monodisperse case $s_c - s_{\mathrm{mix}}$ ($s_{\mathrm{mix}} = 0$ in this case) becomes very nearly zero after the liquid freezes (around $\phi \approx 0.7$), indicating a continuous or a very mildly discontinuous liquid-solid phase transition. More interesting is the fact that $s_c - s_{\mathrm{mix}}$ also becomes nearly zero for the binary glasses around the kinetic phase transition (around $\phi \approx 0.8$). This important observation has not been made before. It means that the estimated number of packings that the liquid samples near the glass transition is very close to s_{mix}, which is also the entropy of the uncorrelated ensemble of discrete states in which a fraction x_A of the particles is chosen to be large and the remaining particles are chosen to be small. It is interesting to observe that the parabolic fit to $s_c(\phi_J)$ from the work in Ref. [15], if constrained to equal the mixing entropy at the maximum, passes through zero at $\phi \approx 0.9$, much higher than the extrapolation in [5] and close to the crystal jamming density. We note that all measurements of s_c in the lit-

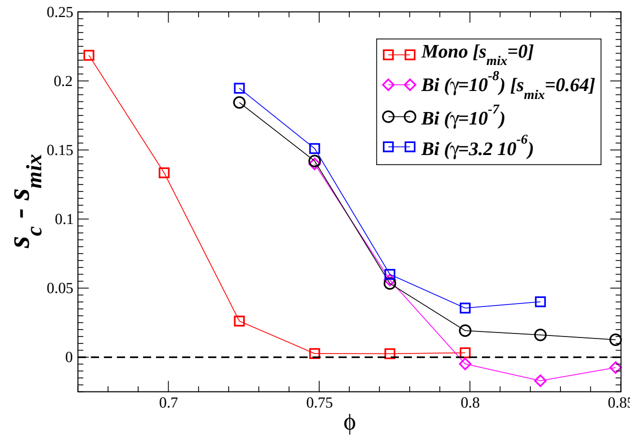


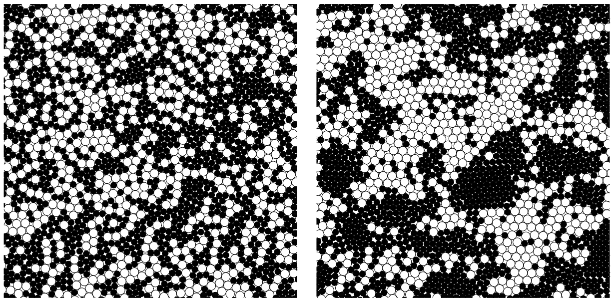
Figure 3: Estimated $s_c(\phi) - s_{\mathrm{mix}}$ for monodisperse and bidisperse systems of $N = 4096$ disks, as obtained from (sufficiently slow) compressions with a range of γ's.

erature that we are aware of are above or close to s_c near the kinetic glass transition, and all estimates of the zero crossing of s_c are based on extrapolations beyond this point without numerical support [5, 6, 7].

Such extrapolations are flawed and, in fact, an exponential number of amorphous jammed packings exist over the whole density range from that accepted as the MRJ density $\phi_{\mathrm{MRJ}} \approx 0.84$ to that of the phase-separated crystal $\phi_{\max} \approx 0.91$. Lower-density jammed packings also exist [15]; however, they do not have thermodynamic significance and thus our simulations do not generate them. In our simulations we observe that higher ϕ_J implies microsegregation in the form of increased clustering of the large particles. This has been most vividly demonstrated in Ref. [13]. This observation suggests that one can generate denser packings by artificially encouraging clustering.

To achieve clustering, we start from a monodisperse ($\kappa = 1$) triangular crystal at pressure $p = 100$ in which a third of the particles has been selected as being "large". The large particles then slowly grow in diameter while the system is kept in (quasi)equilibrium at a constant (isotropic) pressure using a Parinello-Rahman-like variation of the MD algorithm [16]. When $\kappa = 1.4$ we stop the process and then slowly compress the system to jamming. By spatially biasing the initial partitioning into large and small disks, we can achieve a desired level of clustering and higher jamming densities. For this purpose we use a level-cut of a Gaussian random field (GRF) with suitably chosen parameters for a flexible family of pair correlation functions [19]. Figure 4 illustrates two different jammed packings, one with an uncorrelated random choice of large disks, and another with correlations encouraging microsegregation.

To determine the configurational entropy (degeneracy) for a given choice of the GRF parameters, we use a recently-developed algorithm for obtaining numerical approximations of the entropy (per site) of lattice systems [20]. The algorithm numerically measures the probabilities of observing a given configuration, which in our case is the partitioning of the triangular lattice into large and



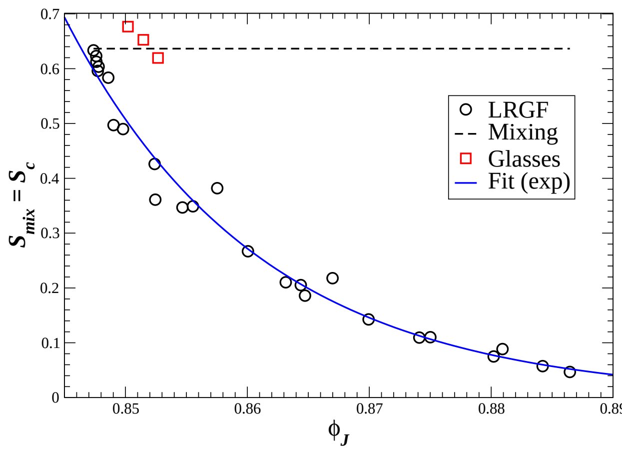


Figure 5: The measured degeneracy of packings of $N = 4096$ disks obtained by using different parameters of a random Gaussian field with Matern correlations [19], as a function of the jamming density. For comparison, we have shown $s_c(\phi = 0.825)$ for the three compressions shown in Fig. 3.

small disks, for small windows (we have used 4×4 windows). This can be done by generating sufficiently many GRF realizations and counting the number of times a given configuration occurs. A Markov expansion is then used to approximate the entropy per site s_c. Figure 5 shows our results for s_c versus the jamming density ϕ_J, for a wide choice of the GRF parameters. The results clearly show that in order to increase ϕ_J one must sacrifice degeneracy (s_c). The figure also shows the first *measured*, rather than extrapolated, estimate of $s_c(\phi_J)$. This observed $s_c(\phi_J)$ only goes to zero for the phase-separated crystal state, rather than the hypothetical amorphous ideal glass state postulated by extrapolations.

Continuing on work in Ref. [2], we explicitly demonstrated that the concept of random close packing as the most-dense jammed amorphous packing is flawed. By trading off degeneracy for density in a continuous manner, we constructed an exponential number of amorphous jammed packings with densities spanning the range from the most disordered to most ordered jammed states. We explicitly calculated, as opposed to extrapolated, the degeneracy entropy for densities well above that of the postulated ideal glass transition, and found that the degeneracy is positive for all "amorphous" states and vanishes only for the phase-separated crystal. For the maximally random jammed state, the found a degeneracy entropy very close to the mixing entropy. Furthermore, our free-energy calculations predict a thermodynamic crystallization well-below the kinetic glass transition, casting additional doubt on the search for a thermodynamic origin of the glass transition. Although the present study focused on the hard-disk binary mixture, the fundamental principles are general enough to be applicable to a host of related systems, notably, both mono- and bi-disperse with hard-core and soft interactions.

This work was supported in part by the National Science Foundation under Grant No. DMS-0312067.

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